PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/386, 3/38, D06M 15/15, 16/00	A1	(11) International Publication Number: **WO 98/00500** (43) International Publication Date: 8 January 1998 (08.01.98)

(21) International Application Number: PCT/EP97/03371

(22) International Filing Date: 24 June 1997 (24.06.97)

(30) Priority Data:
9613758.3 1 July 1996 (01.07.96) GB

(71) Applicant *(for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only)*: UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant *(for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW)*: UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(72) Inventors: JONES, Christopher, Clarkson; 4 Birchridge Close, Spital, Wirral L62 2EF (GB). PERRY, Amanda; 109 The Oval, Ellesmere Port, Cheshire L65 9AT (GB).

(74) Agent: MOLE, Peter, Geoffrey; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DETERGENT COMPOSITION

(57) Abstract

A composition comprising a peptide or protein Deposition Aid having a high affinity for fibres or a surface and attached/adsorbed to the peptide or protein deposition aid a benefit agent. The composition effectively deposits the Benefit Agent onto fabric during the wash cycle.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DETERGENT COMPOSITION

Technical Field

The present invention relates to a detergent composition and to a process for adding Benefit Agents during the wash, in particular the invention relates to detergent compositions containing a new form of deposition system based on agents with a high affinity for a fabric.

Background of the Invention

It is well known and well documented in the relevant technical and patent literature that fibrous materials such as fabrics or the like can be treated with Benefit Agents which deliver one or more desirable properties to the material.

Conventionally these treatments are carried out by applying to the surface of the material a composition containing one or more active ingredients which serve to impart the benefit or benefits which are wanted.

The application of such conventional Benefit Agents compositions to achieve the desired results relies essentially on two key factors: firstly, it is important that the active ingredient or ingredients with which the substrate is to be treated are provided in a form of composition which on the one hand is stable upon storage and maintains the essential Benefit Agent or aids in active form, and on the other hand allows the active(s) to be deposited from the composition onto the substrate surface; secondly, it is essential that once deposited the Benefit Agent or aids are retained on the substrate surface, so that when the treatment

is completed and for example the substrate is rinsed to remove unwanted excess composition or residual components thereof, sufficient of the Benefit Agent remains attached to the substrate surface so as to impart the intended characteristic benefit or benefits thereto.

This attachment of active material to the treated substrate surface is generally of the nature of physisorption; that is to say, the Benefit Agents are adsorbed onto the surface of the substrate by virtue of physical intermolecular forces such as hydrogen bonding. Conventionally, it has been accepted that this form of retention of active substrates on treated substrate surfaces gives adequate results as regards achievable benefits and economics.

However, the deposition of Benefit Agents in such a manner is poor and there is a need to improve the efficiency of the deposition. There is also a need to ensure that the Benefit Agents, remain on the fabric or fibre during additional steps such as rinsing and during wear.

The present application has derived a way of overcoming this problem of depositing Benefit Agents onto fabrics, and ensuring that they remain on the fabric during wear.

Definition of the Invention

Accordingly the present application relates to a composition comprising a peptide or protein Deposition Aid having a high affinity for fibres or a surface and a Benefit Agent attached/adsorbed to the peptide or protein Deposition Aid.

The present application also relates to a method of treating a fibre or surface with a Benefit Agent comprising the steps of:

i) selecting a Benefit Agent attached/adsorbed to a peptide/protein Deposition Aid;

ii) applying the Benefit Agent-peptide/protein Deposition Aid to the fibre or surface

The present application further relates to the use of a peptide/protein to deposit a Benefit Agent onto a fibre, wherein the Benefit Agent is attached/adsorbed to the peptide/ protein and the peptide/protein has an affinity for said fibre.

The application also relates to a process for attaching a Benefit Agent to a peptide/protein Deposition Aid. The process comprises the steps of:

i) reacting the Benefit Agent to a linking agent;

ii) reacting the linking agent with the peptide/protein Deposition Aid.

Steps i) and ii) may be reversed.

The present application further relates to a Benefit Agent peptide/protein deposition aid produced by the above process.

Detailed Description

The Peptide/Protein Deposition Aid

The peptide/protein Deposition Aid is any material that has a high affinity for fibres or a surface.

One preferred embodiment is that the peptide/protein Deposition Aid is an enzyme. Preferred enzymes are cellulases, lipases, proteases, or cutinases or keratinases. Cellulases are especially preferred.

A second preferred embodiment is that the peptide/protein Deposition Aid is the binding domain of the above enzymes. It may also be advantageous if the peptide/protein Deposition Aid is a peptide/protein which although not an enzyme has a similar or identical structure to that of a binding site of an enzyme, and thus has a similar function. In the context of this invention a similar structure is defined as a sequence of amino acids which conserve the binding affinity of the binding site. In this context it is preferred that the binding site which the peptide/protein represents is the binding site of the enzymes cellulase, lipase, cutinase, keratinase or protease. It is especially preferred if the binding site is that of cellulase, in particular the cellulose binding domain (C.B.D.).

The Benefit Agent

A Benefit Agent is described in the context of this invention as any compound which gives a desirable effect on a fibre, fabric or surface.

It is especially preferred if the benefit agent gives a perceivable benefit to the fabric.

The present invention is of particular use when the composition is used in laundering fabrics and in this context a Benefit Agent can be defined as any agent which effects the feel, appearance, or the perception of a fabric. It is particularly preferred if the Benefit Agent is a fabric softening agent, a perfume, a polymeric lubricant, a photo protective agent (such as a sunscreen), a latex, a resin, a dye fixative agent, an encapsulated material, an antioxidant, an insecticide, a soil repelling agent, a soil release agent.

If the Benefit Agent is a fabric softening agent it preferably comprises a clay, a cationic active, or silicone.

Suitable clays include a three layered smectite clay, preferably having a cation exchange capacity as described in GB1400898 (Procter and Gamble). Especially preferred are clays which are 2:1 layer phyllosilicates possessing a lattice charge deficiency in the range of 0.2 to 0.4g equivalents per half unit cell as described in EP 0 350 288 (Unilever).

Suitable cationic softening agents include quaternary ammonium softening compounds having a solubility in water at pH 2.5 and 20°C of less than 10g/l.

It is particularly advantageous if the cationic softening compound is a quaternary ammonium compound in which at least one long chain alkyl group is connected to the quaternary ammonium group via at least one ester link. Suitable cationic softeners are described in US 4 137 180 (Naik) and WO 93/23510 (P&G).

If the Benefit Agent is a polymeric lubricant it may be any polymeric lubricant suitable for softening a fabric. Suitable lubricants include silicones in particular those disclosed in GB 1549 180 (P&G), EP 459 821 (Unilever) and EP 459 822 (Unilever).

The Benefit Agent may be a soil release polymer, suitable soil release polymers include polyesters of terephthalic acid and other aromatic dicarboxylic acids. Soil release polymers that may be used with the present invention which are the condensation products of aromatic dicarboxylic acids and dihydric alcohols include EP 185 427A, EP 241 984A, EP 241 985A and EP 272 033A (Procter & Gamble). Particularly preferred are the so called PET/POET (polyethylene terephthalate/polyoxyethylene terephthalate) and PET/PEG (Polyethylene terephthalate/ polyethylene glycol) which are disclosed in US 3 557 039 (ICI), GB 1 467 098 and EP 1 305A (Procter & Gamble). Polymers of this type are available commercially, for example, as Permalose, Aquaperle and Milease (Trade Marks, ICI) and Repel-O-Tex SRP3 (Trade Mark, Rhône-Poulenc). Sulphonated non-end-capped polyester of terephthalic acid, isophthalic acid, sulphoisophthalic acid and ethylene glycol as described in PCT/FR95/00658 (Rhône-Poulenc), published 1 December 1995 and sold commercially as Gerol (Trade mark Rhône-Poulenc) are also advantageous when used in conjunction with the present invention.

Latex materials are also defined as Benefit Agents. A latex is defined as a material suitable for improving the drape of fabric, suitable materials include a polyvinylacetate homopolymer such as 9802 (Vinamul).

Benefits aids may also include resins such as Knittex BE (Ciba-Geigy) or silicas such as Crosanaol NS (Crosfield), these Benefit Agents prevent pill formation on the fabric.

The Benefit Agent may be any material which is encapsulated. Suitable encapsulating materials include starches and poly(vinylacetate) and urea/formaldehyde condensate based materials.

Suitable materials that may be encapsulated include perfumes, insect repellents, fungicides, or photo protective agents.

The Benefit Agent is attached/adsorbed to the peptide/protein Deposition Aid. If the Benefit Agent is adsorbed this is preferably by simple physisorption of the enzyme.

If the benefit is attached to the peptide/protein Deposition Aid this is preferably via a linking agent.

Suitable linking agents are molecules which show a high affinity for the Benefit Agent. It is preferred if the linking agent is covalently attached to the peptide/protein Deposition Aid, it is also advantageous if the linking agent is covalently bound to the Benefit Agent.

Preferred linking agents are selected from 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, N-ethyl-5-phenylisoxazolium - 3 - sulphonate, 1 - cyclohexyl-3-(2

morpholinoethyl) carbodide metho-p-tolune sulphonate, N-ethoxycarbonyl-2-ethoxy 1,2 dihydroquinoline or glutaraldehyde.

Detergent Active Compounds

The detergent compositions of the invention will contain, detergent-active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

The detergent compositions of the invention may contain anionic surfactants. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl benzene sulphonates, alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates, alkyl ether carboxylates, alkyl sarccosinates. Sodium salts are generally preferred.

The compositions of the invention may also contain nonionic surfactant.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of

ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The choice of detergent-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or nonionic surfactant, or combinations of the two in any ratio, optionally together with soap.

Detergency Builders

The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:

$$0.8\text{-}1.5\ Na_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium

aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Bleach Components

Detergent compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and

pernonanoic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever) are also of great interest. The cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) may also be used.

The bleach system can be either supplemented with or replaced by a peroxyacid. Examples of such peracids can be found in US 4 686 063 and US 5 397 501 (patent on TPCAP - Unilever). A preferred example is the imido peroxycarboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phtalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These Bleach stabilisers are also useful for stain removal, especially in products containing low levels of bleaching species or no bleaching species.

An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

Enzymes

Suitable enzymes which may be used with the peptide/protein Deposition Aid of this invention include the proteases, amylases, cellulases, oxidases, peroxidases, lipolases and lipases cutinases and ceratinases usable for incorporation in detergent compositions.

Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark) (obtainable from Showa-Denko of Japan), Optimase (Trade Mark) (from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark) (obtainable from Pfizer of U.S.A.).

Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%.

Other ingredients

The compositions of the invention may contain alkali metal, preferably sodium, carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate.

One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; fabric softening compounds, soil release polymers, fluorescers and decoupling polymers. This list is not intended to be exhaustive.

The detergent composition when diluted in the wash liquor (during a typical wash cycle) will give a pH of the wash liquor from 7 to 10.5.

The detergent components of the present invention may be incorporated in detergent compositions of all physical types, for example, powders, liquids, gels and solid bars.

Detergent compositions of the invention may be prepared by any suitable method.

Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l.

Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used.

Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to

the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

EXAMPLES

The invention will now be illustrated by with reference to the following examples.

Example 1: Demonstration of the preparation and deposition of the cellulase latex system

Particles of 0.5µm polystyrene latex (ex Polyscience) were taken and the surface functionalised to have free carboxylate groups. The bulk of the particles have small amounts of fluorescent dye incorporated.

All reactions took place in 2ml Eppendorf microcentrifuge tube at room temperature.

1) A 0.5ml portion of 2.5% latex was taken and rinsed three times with 1.5 ml of 0.01M carbonate buffer at pH 9.6 (Centrifuge, decant, resuspend).

2) The latex was rinsed a further three times using 0.02M phosphate buffer at pH 6.0.

3) The latex was resuspended in 0.6ml of phosphate buffer then added to 0.6ml of 2% 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride and allowed to react for 3 hours, centrifuged and decanted.

4) The resulting compound was rinsed three times in 1.5 ml of 0.2M borate buffer at pH8.5, and resuspended in borate buffer followed by addition of 0.3 ml of a solution containing 160 µg of cellulase obtained from Trichoderma reesei in borate buffer. The reactants use left to react overnight.

5) 20µl of 0.25M ethanolamine was added for one hour to react with any unreacted coupling sites.

6) The dispersion was centrifuged and resuspended in 1ml of borate buffer.

Treatment of Cotton

The resulting mixture was used to treat cotton as follows

1) Two 5x5cm squares of white cotton were added to 38 ml of liquor containing 0.001 mol / l carbonate buffer at pH 9.6, 1 g / l of a surfactant system comprising 50% PAS, 35% Synperonic A7 and 15% Synperonic A3 and 5.0 ppm of the fluorescent latex. Two conditions were examined:

   i) unmodified latex
   ii) cellulase-modified latex

2) The cloths were agitated in the liquor for 3 hours then removed and air dried

3) The percentage of latex deposited was determined by comparing the fluorescence of the liquor before addition of the cloth to that after removal of the cloth. The results are shown in Table 1.

Table 1

Latex	% deposited
unmodified	0.2%
Cellulase-modified	10.7%

Example 2; Demonstration of the use of the cellulase deposition system to deliver an anionic fabric conditioner to cotton.

A 5% solids dispersion was prepared, where the particles consisted of a surfactant mesophase of composition (by mole fraction) 0.55 octadecanol: 0.40 cetyl sodium sulphonate : 0.05 stearic acid.

Cellulase obtained Trichoderma reesei was covalently attached to the particles using the following method:

1) 10g of the 5% dispersion was added to 10ml of 0.02 mol / l phosphate buffer at pH 6.5

2) To the mixture was added 0.48ml of 2% 1-ethyl-3-(dimethylaminopropyl) carbodiimide hydrochloride and allowed to react for three hours

3) pH was raised to 8.5 by addition of 1 mol / l sodium hydroxide

4) 1ml of a solution containing 5 mg of cellulase from Trichoderma reesei in 0.2 mol/l borate buffer at pH 8.5 was added and allowed to react overnight

5) 20 µl of 0.25 mol/l ethanolamine was added to react with any unreacted coupling sites.

The resulting mixture was used to treat cotton Terry towelling sheets to demonstrate an antiharshening benefit

1) 40g of 20x20cm Terry Towelling squares were added to 1000 ml of liquor in a Tergotometer pot at ambient temperature. Three different liquors were examined:

   i) water only
   ii) water plus 4 g/l of the unmodified dispersion
   iii) water plus 4 g/l of the cellulase-modified dispersion

2) The cloths were agitated at 60 rpm for 30 minutes

3) Cloths were removed, given a 1 minute spin dry and then air dried

4) The harshness of the cloths was measured using an in-house Harshness Meter. The results are shown in Table 2

Table 2

Cloth	Harshness
Untreated cloth	409 ± 13
water only	451 ± 10
water plus unmodified dispersion	442 ± 14
water plus cellulase modified dispersion	413 ± 14

Example 3; Comparing the use of physisorbed cellulase with covalently bound cellulase to deliver latex particles to cotton.

All preparations took place in 2 ml Eppendorf microcentrifuge tube at room temperature. The latex used was a 2.5% dispersion of 0.5 µm polystyrene latex particles whose surface has carboxylate groups incorporated. The latex has a small amount of fluorescer incorporated.

1) A 0.5 ml portion of 2.5% latex was taken and rinsed three times with 1.5 ml of 0.1 M carbonate buffer at pH 9.6 using a centrifuge, decant, resuspend technique.

2) The latex was rinsed three times in 1.5 ml of 0.2 M borate buffer at pH 8.5, and resuspended in borate buffer followed by addition of 0.3 ml of a solution containing 160 µg of cellulase obtained from Trichoderma reesei in borate buffer. The dispersion was left overnight for the cellulase to adsorb.

3) The dispersion was centrifuged and resuspended in 1 ml of phosphate buffer.

Treatment of Cotton

The resulting mixture was used to treat cotton as follows;

1) Two 5 x 5 cm squares of white cotton were added to 38 ml of liquor containing 0.01 mol / l phosphate buffer at pH 7.0 and 5 ppm of the fluorescent latex. Three conditions were examined:

i) unmodified latex
ii) latex with covalently attached cellulase prepared as described in Example 1
iii) latex with physisorbed cellulase prepared as described in this example

2) The cloths were agitated in the liquor for 3 hours then removed and air dried.

3) The percentage of latex deposited was determined by comparing the fluorescence of the liquor before addition of the cloth to that after removal of the cloth. The results are shown in Table 3.

Table 3

Latex	% deposited
unmodified	6.8%
Cellulase covalently attached	89.6%
Cellulase physisorbed	61.9%

Example 4; Demonstration that enhanced delivery to cotton can be achieved using a variety of deposition aids.

A number of latex dispersions were prepared each having a different cellulase enzyme covalently attached according to the method described in Example 1. Four different cellulases were used:

i) cellulase from Trichoderma reesei

ii) cellulase EG2 from Trichoderma longibrachiatum
iii) cellulase EG3 from Trichoderma longibrachiatum
iv) cellulase E5 from Thermonospora fusca

The latices were used to treat cotton according to the method described in Example 3. The results are shown in Table 4.

Table 4

Latex	% deposited
unmodified	5.2
modified with cellulase from Trichoderma reesei	65.2
modified with EG2 from Trichoderma longibrachiatum	55.7
Modified with EG3 from Trichoderma longibrachiatum	15.6
Modified with E5 from Thermonospora fusca	34.5

Example 5; Demonstration of the use of the cellulase deposition system to deliver a silicone fabric softener to cotton

1) 2.5 g of a carboxylated silicone (TP502 from Union Carbide) was dispersed in 2.5 g of 0.02 M pH 6.5 phosphate buffer.
2) 2.5 g of 1-ethyl-3-(dimethylaminopropyl) carbodiimide hydrochloride in 2.0 ml of 0.02 M pH 6.5 phosphate buffer was added dropwise to the silicone dispersion. The mixture was agitated for 3 hours on a bottle roller.
3) Sodium hydroxide was added to raise the pH to 8.5
4) 0.032 g of cellulase from Trichoderma reesei in 1.0 ml of 0.2 M pH 8.5 borate buffer was added to the dispersion. This was agitated overnight on a bottle roller
5) 4 ml of 0.25 M ethanolamine was added and mixed for 1 hour

Treatment of Cotton

The cellulase-modified silicone was incorporated into a model wash and a model rinse. In each case two controls were also used: incorporation of unmodified silicone and the use of no silicone at all. The fabrics used in the experiments were 20 x 20 cm squares of white Terry towelling. The model washes and rinses were performed in a Tergotometer using the following protocols:

Rinse

1 litre of demineralised water was added to a Tergotometer pot. If used, 0.2 g of the appropriate silicone was added. The liquor was maintained at ambient temperature. 40 g of the 20 x 20 cm squares of Terry towelling were added to the

pot which was then agitated at 60 rpm for 5 min. The cloths were then spun dry for 30 s in a domestic spin drier and finally line dried.

Wash

1 litre of demineralised water was added to a Tergotometer pot. This was kept at a constant 40°C. 1 g of LAS (Petrelab 550, sodium salt) was added and, if used, 0.2 g of the appropriate silicone. 40 g of the 20 x 20 cm squares of Terry towelling were added to the pot which was then agitated at 60 rpm for 30 min. The cloths were given 2 x 5 min rinses in demineralised water then spun dry for 30 s in a domestic spin drier and finally line dried.

Evaluation

The cloths were then evaluated, both instrumentally using an in-house Harshness meter and by a panel using a round-robin paired comparison protocol where each cloth is judged against every other cloth. The results are given in Table 5

Table 5

Conditions	Harshness score	Panel Preference score
rinse containing no silicone	266 ± 5	0.069
rinse containing unmodified silicone	265 ± 8	0.096
rinse containing cellulase-modified silicone	236 ± 4	0.610
wash containing no silicone	281 ± 5	0.057
wash containing unmodified silicone	286 ± 4	0.057
wash containing cellulase-modified silicone	272 ± 8	0.111

In the case of both the wash and the rinse treatment, the panel judged the treatment containing the cellulase-modified silicone to deliver greater softness than the two controls.

In each case this was statistically significant at the 95% confidence level

Example 6; Demonstration of the use of the cellulase deposition system to deliver a cationic surfactant fabric softener from a wash containing anionic surfactant.

5 g of a mixture consisting of 85% 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride, 8% stearic acid and 7% propylene glycol was melted at 80°C and then added to 95 g of distilled water at 80°C accompanied by

vigourous stirring. The mixture was cooled to ambient temperature while maintaining the stirring and resulted in a fine dispersion of the material in water. 50 g of this dispersion was added to 50 ml of 0.02 M pH 6.5 phosphate buffer and mixed to form a homogeneous dispersion. 3.53 ml of 2% 1-ethyl-3-(dimethylaminopropyl) carbodiimide hydrochloride in 0.02 M pH 6.5 phosphate buffer was added dropwise to the dispersion. This was agitated for 3 hours on a bottle roller at ambient temperature. Sodium hydroxide solution was then added to raise the pH to 8.5. 0.1 g of cellulase from Trichoderma reesei in 1 ml of 0.2 M pH 8.5 borate buffer was added. The mixture was agitated overnight on a bottle roller at ambient temperature. 0.1 ml of 0.25 M ethanolamine was added and the mixture agitated for 1 hour.

Treatment of Cotton

The cellulase-modified dispersion was incorporated into a model wash. Two controls were also used: incorporation of unmodified dispersion and the use of no cationic surfactant dispersion at all. The fabrics used in the experiments were 20 x 20 cm squares of white Terry towelling. The model washes were performed in a Tergotometer using the following protocol:

Wash

1 litre of demineralised water was added to a Tergotometer pot. This was kept at a constant 40°C. 1 g of LAS (Petrelab 550, sodium salt) was added and, if used, 0.2 g of the appropriate cationic surfactant dispersion. 40 g of the 20 x 20 cm squares of Terry towelling were added to the pot which was then agitated at 60 rpm for 30 min. The cloths were given 2 x 5 min rinses in demineralised water then spun dry for 30 s in a domestic spin drier and finally line dried.

Evaluation

The cloths were then evaluated, both instrumentally using an in-house Harshness meter and by a panel using a round-robin paired comparison protocol where each cloth is judged against every other cloth. The results are given in Table 6.

Table 6

Conditions	Harshness score	Panel Preference score
unwashed fabric	263 ± 6	0.152
cationic-free wash	270 ± 10	0.067
wash containing unmodified cationic	291 ± 10	0.122
wash containing cellulase modified cationic	259 ± 7	0.658

The panel judged the cloths washed with a formulation containing the cellulase-modified cationic surfactant dispersion to be softer than the two controls. The panel also judged that this treatment had rendered the fabric softer than it was before undergoing the wash. These panel results were significant at the 95% confidence level.

Example 7; Demonstration of the use of glutaraldehyde as a linking agent.

For this work a sample of a 0.5 µm polystyrene latex having a surface containing free amine groups was obtained from Sigma. The latex also contained a small amount of a fluorescent dye.

Two modified latices were prepared using different levels of cellulase.

1) 1.0 ml of a 2.5% dispersion of the latex was placed in an Eppendorf tube.
2) The latex was washed three times with 1.5 ml portions of phosphate buffered saline using a centrifuge / decant / resuspend technique.
3) The final pellet was resuspended in 8% glutaraldehyde solution and agitated overnight at ambient temperature.
4) The pellet was then washed a further three times using phosphate buffered saline.
5) Either 160 µg or 500 µg of cellulase from Trichoderma reesei was added to the dispersion and agitated for five hours at ambient temperature.
6) The dispersion was centrifuged and the pellet resuspended in 1.0 ml of 0.5 M ethanolamine and then agitated for 30 minutes at ambient temperature.
7) The latex was centrifuged and finally resuspended in 1.0 ml of phosphate buffered saline.

Treatment of Cotton

The resulting mixture was used to treat cotton as follows

1) Two 5 x 5 cm squares of white cotton were added to 38 ml of liquor containing 0.01 mol / l carbonate buffer at pH 9.6 and 15 ppm of the fluorescent latex. Three conditions were examined:

    i) unmodified latex
    ii) latex modified with low level of cellulase
    iii) latex modified with high level of cellulase.

2) The cloths were agitated in the liquor for 3 hours then removed and air dried

3) The percentage of latex deposited was determined by comparing the fluorescence of the liquor before addition of the cloth to that after removal of the cloth. The results are shown in Table 7.

Table 7

Latex	% deposited
unmodified	19%
modified with low level of cellulase	38%
modified with high level of cellulase	65%

CLAIMS

1. A composition comprising a peptide or protein Deposition Aid having a high affinity for fibres or a surface and a Benefit Agent attached/adsorbed to the peptide or protein Deposition Aid.

2. A composition according to claim 1 in which the Benefit Agent is attached to the peptide/protein Deposition Aid via a linking group

3. A composition according to claim 1 or claim 2 in which the linking group is covalently bound to the peptide/protein Deposition Aid.

4. A composition according to any preceding claim in which the linking group is selected from 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, N-ethyl-5-phenylisoxazolium-3-sulphonate, 1-cyclohexyl-3-(2-morpholinoethyl) carbodiiide metho-p-tolune sulphonate, N-ethoxycarbonyl-2-ethoxy 1,2 dihydroquinoline or glutaraldehyde.

5. A composition according to any preceding claim in which the Deposition Aid is a protein.

6. A composition according to any preceding claim in which the Deposition Aid is an enzyme.

7. A composition according to claim 6 in which the enzyme is selected from cellulase, lipolase, lipase, protease, cutinase or keratinase.

8. A composition according to anyone of claims 1 to 3 in which the peptide/protein Deposition Aid is not an enzyme but has a chemical structure similar or identical in structure to that of a binding site of an enzyme.

9. A composition according to claim 7 in which the peptide/protein Deposition Aid has a chemical structure similar or identical to the binding site of the enzymes cellulase, lipase or protease.

10. A composition according to any preceding claim in which the Benefit Agent is selected from a perfume, an encapsulated perfume, photo protective agent, a soil release polymer, a soil repelling agent, a fabric softening compound, an insecticide, a fungicide, antioxidants, or dye fix actives.

11. A composition according to any preceding claim which further comprises a detergent surfactant.

12. A composition according to claim 11 in which the detergent surfactant is a nonionic surfactant.

13. A method of treating a fibre or surface with a Benefit Agent comprising the steps of:

i) selecting a Benefit Agent attached/adsorbed to a peptide/protein Deposition Aid;

ii) applying the Benefit Agent-peptide/protein Deposition Aid to the fibre or surface.

14. A method according to claim 13 in which the fibre or surface is a fabric.

15. A method according to claim 13 in which the method of applying the Benefit Agent-peptide/protein deposition aid to the fibre or surface the fabric or surface with a composition comprising said Benefit Agent and peptide/protein Deposition Aid.

16. Use of a peptide/protein to deposit a Benefit Agent onto a fibre wherein the Benefit Agent is attached/adsorbed to the peptide/protein and the peptide/protein has an affinity for said fibre.

17. A process for attaching a Benefit Agent to a peptide/protein Deposition Aid comprising the steps of:

i) reacting the Benefit Agent to a linking agent;

ii) reacting the linking agent with the peptide/protein Deposition Aid.

18. A process for attaching a Benefit Agent to a peptide/protein Deposition Aid comprising the steps of:

i) reacting the linking agent with the peptide/protein Deposition Aid.

ii) reacting the benefit agent to a linking agent.

19. A Benefit Agent peptide/protein deposition and produced according to the process of either of claims 17 or 18.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/03371

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386 C11D3/38 D06M15/15 D06M16/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 041 150 A (KARJALA SULO A) 9 August 1977 see column 4, line 7 - line 32 ---	1-3,5, 8-10, 13-19
A	DATABASE WPI Section Ch, Week 9405 Derwent Publications Ltd., London, GB; Class A23, AN 94-039714 XP002044326 & JP 05 344 897 A (AMANO PHARM KK) , 27 December 1993 see abstract --- -/--	1-19

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

2

Date of the actual completion of the international search	Date of mailing of the international search report
22 October 1997	04.11.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Blas, V

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/03371

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91 16424 A (GEYER HANS ULRICH ;KONIECZNY JANDA GERHARD (DE)) 31 October 1991 see page 3, last paragraph - page 4 see page 16, last paragraph - page 17	1-19
A	EP 0 687 729 A (KAO CORP) 20 December 1995 see the whole document	1-19
A	US 5 494 744 A (EVERHART DENNIS S ET AL) 27 February 1996 see column 13, line 37 - line 47	1-19
A	US 4 432 888 A (CIOCA GHEORGHE) 21 February 1984 see the whole document	1-19
A	WO 96 17929 A (NOVONORDISK AS ;OLSEN ARNE AGERLIN (DK); HANSEN LARS BO L (DK); BE) 13 June 1996 see the whole document	1-19

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 97/03371

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4041150 A	09-08-77	CA 988427 A	04-05-76
WO 9116424 A	31-10-91	DE 4013142 A	31-10-91
EP 0687729 A	20-12-95	JP 8003874 A	09-01-96
		JP 8269873 A	15-10-96
		US 5593779 A	14-01-97
US 5494744 A	27-02-96	AU 3323995 A	06-05-96
		EP 0786028 A	30-07-97
		WO 9612058 A	25-04-96
		ZA 9507637 A	22-04-96
US 4432888 A	21-02-84	NONE	
WO 9617929 A	13-06-96	AU 4114496 A	26-06-96
		EP 0796324 A	24-09-97
		FI 972443 A	09-06-97